NIRT: Molecular Assembly for Hybrid Electronics

NSF NIRT (or NSEC) Grant 0304122

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Introduction

The reduction of feature size on chips achieved by the tremendous technological advances in miniaturization that have enabled more and more transistors to be packed onto a silicon chip is limited not just by the resolution of the beam optics and resist chemistry, but also by the problem of inevitable fluctuations, both quantum and classical. Consequently, below a limiting dimension that we have nearly reached, a new paradigm that goes beyond conventional solid state electronics has to be developed for the next generation of electronics devices. Our approach is to adopt a new biologically-inspired approach called "Self-Evolving Neuromorphic Networks" [1]. This realization has in part been a result of recent observations by neurobiologists that certain functions of the neocortex (the part of the brain responsible for the most advanced information processing functions including complex image recognition and self-awareness) may be understood on the basis of "synaptic Darwinism". This assumes that neural cell connections (synapses) are in a state of permanent change: under the effect of brain activity some synapses are discretely strengthened, while others die out–the process paralleled to mutations at evolution. This observation may be used as the basis for artificial models of the neocortex in the hope that most (if not all) of their useful structuring may be achieved by natural synaptic evolution, provided that the synapse devices are sufficiently adaptive ("plastic"), and the model speed is sufficiently high to make the evolution time scale reasonable.

Such modeling, however, cannot be achieved using the CMOS VLSI circuit technology simply because of the necessary synapse density. Indeed, each synaptic device would require, as a minimum, not only a connecting transistor, but also at least one memory cell for long-term storage of the synaptic weight. A resolution of this problem may come from a more recent finding, in the field of single-electronics. In previous work [2], we have managed to show that very simple single-electron devices may serve as effective "switching latches" playing the role of single-bit-weight, analog-signal (BiWAS) synapse. Since a single molecule has a much smaller area, therefore larger packing densities can be theoretically obtained. The advantage to "neuromorphic" networks is that we have shown that these networks are not as affected by the fluctuations inherent to single-electron devices. In fact, they exploit slow time-dependent fluctuations. Their high parallelism and intrinsic redundancy allow the individual elements to have a distribution of parameters. However, a serious limitation in the development of neuromorphic networks is that there is a very slim chance for the extension of the usual patterning techniques (including extreme ultraviolet, e-beam, and X-ray lithographies) to the packing densities required by these networks. A possible solution to this problem is to use the process of molecular self-assembly in order to assemble these circuits. In order for this to succeed, however, the random aspect of molecular self-assembly has to be carefully understood and controlled. At present, there is no detailed understanding of the process of assembling these molecular circuits. It is this crucial gap that we address in this proposal. The goal of this proposal is therefore twofold:

1) To develop theoretical models that will predict the process of self-assembly in order to create "neuromorphic" networks, and determine the parameters that control the electronic transport properties of such systems

2) To propose new technologies based on the experimental realization of the theoretical models

Research Methodology

We have divided the proposed work into a series of areas: *System architecture* and *properties*, *Molecular synthesis* and *Molecular assembly*. Since the parameters of the molecular assembly process are set by the demands of the architecture (such as the density of packing, and the electrode spacing and geometry) and the ability of the synthesis
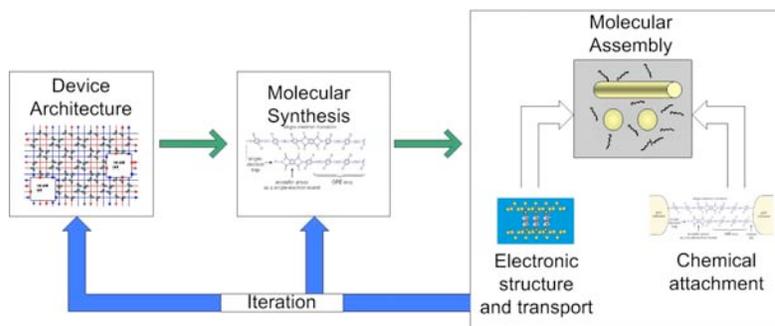

Fig 1: Schematic flowchart of the research methodology

techniques to produce molecules with the desired characteristics, our schematic of the project is shown in the figure below (Figure 5). The goal of the study of molecular assembly is thus to develop clear guidelines that will provide the chemical synthesis with a series of target molecules that can best serve the demands of a molecular synapse, while simultaneously providing limits to the operation of the device based on the transport properties and the attachment of the molecular synapses.

The study of the process of molecular assembly forms the core of this proposal. It consists of two main parts: A microscopic approach which studies the electronic structure, attachment and transport properties of the molecule, and a nanoscopic and mesoscopic study of the process by which these molecules form the molecular circuits necessary for the operation of the "neuromorphic" networks. In the sections below we present recent advances made in this project.

Recent Results

Microscopic studies of attachment by molecules to surfaces: We used Density functional theory (DFT) to study how the isocyanides HNC and CH3NC attach to the gold (111) surface [3]. Isocyanides are recently receiving some attention in molecular electronics applications, but theoretically they have not been studied to the extent that thiolated molecules have been. In order to see if isocyanides can serve as suitable attachment candidates we initiated a series of calculations. We found that these molecules can be adsorbed only at the top site (in contrast with thiolated molecules, which can be adsorbed at any position, with some positions more energetically favorable). The adsorption energy for 1/3 coverage is similar for the two molecules and is rather small (0.18 eV for HNC and 0.22 eV for CH3NC), confirming the general assumption that isocyanides form weaker bonds with gold than do thiolates. A figure showing the preferred orientation of the molecule is shown in Figure 2.
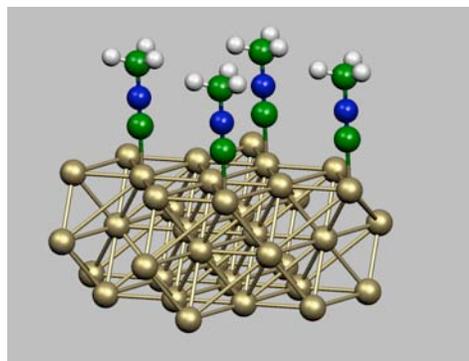

Fig 2: An isocyanide molecule attached to a gold cluster

To improve the quantitative accuracy of DFT calculations for small ionic molecules and clusters, we have also developed a direct derivation for the primary contribution of to the vibrational polarizability for molecules, clusters and other finite systems [4]. The vibrational polarizability is then calculated within the generalized gradient approximation to the density functional theory for a variety of molecules and clusters. The agreement between theory and experiment is quite good.

Transport properties of molecular switches: In the course of our work on theory of electron transport through special organic (naphthalene diimide) molecules designed by Prof. A. Mayr to work as single-electron transistors in hybrid nanoelectronic circuits, we have carried out electron structure calculations for several redox states (n = 0, ±1) of these molecules. The calculations have confirmed that diimide groups of these molecules can really work as a effective acceptor, i.e. the molecular analog of single-electron island, with the effective electron addition energy close to 3 eV. This is sufficient for good operation of the transistor at room temperature. Figure 3 shows the LUMO and HOMO levels in such a molecule.
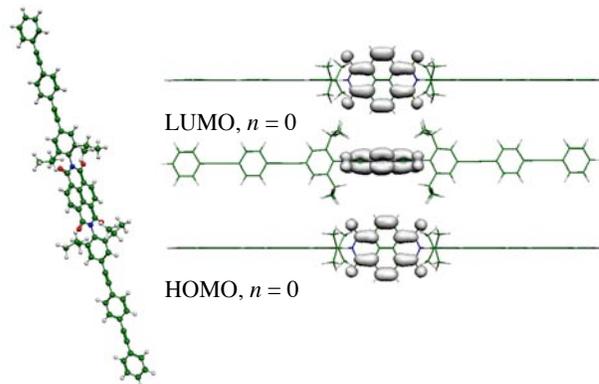

Fig 3: HOMO and LUMO levels in a molecular switch

Mesoscopic models of self-assembly of molecular switches: We have used a mean field mesoscopic model to predict conditions that will allow a molecular switch to connect two electrodes. We use a Rotational Isomeric Scheme model [5] to describe the chain statistics and can vary the persistence length of the molecule, the distance between the electrodes, the aspect ratio of the electrodes and the concentration of molecules. Our results allow us to calculate a phase diagram of
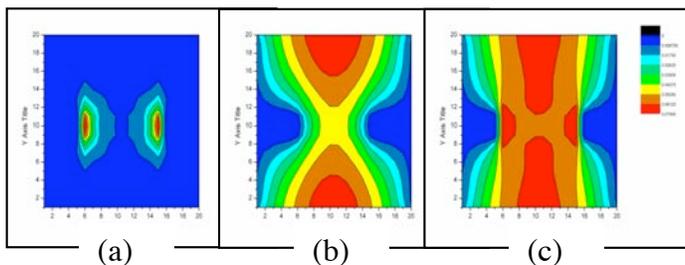

Fig 4: Volume fraction profiles of chain between two electrodes a) adsorbed on a single electrode b) adsorbed on a electrode but not spanning c) spanning the two electrodes.

"connectedness" as a function of all these parameters. In Fig 4, we plot the volume profiles of the chain, illustrating 3 cases: a) where there is strong adsorption at the electrode, b) where the chain is attached to only a single electrode, and c) where the chain connects the electrodes.

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6) For further information please contact dilip.gersappe@sunysb.edu